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(21) International Application Number: PCT/US00/11021 (22) International Filing Date: 24 April 2000 (24.04.00) (30) Priority Data: 09/299,392 27 April 1999 (27.04.99) US (63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 09/299,392 (CON) Filed on 27 April 1999 (27.04.99) (71) Applicant (for all designated States except US): PHILLIPS PETROLEUM COMPANY [US/US]; 4th and Keller, Bartlesville, OK 74004 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BERGMEISTER, Joseph, H. [US/US]; 1024 Grandview Road, Bartlesville, OK 74006 (US). KIMBLE, James, B. [US/US]; 624 Kenwood Dr., Bartlesville, OK 74006 (US). (74) Agents: RICHARDS, John; Ladas & Parry, 26 West 61st Street, New York, NY 10023 (US) et al.		(81) Designated States: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: HYDROCARBON HYDROGENATION CATALYST AND PROCESS (57) Abstract A hydrogenation process in which a hydrocarbon-containing fluid containing a highly unsaturated hydrocarbon such as a diolefin and/or an alkyne is contacted, in the presence of hydrogen and a sulfur impurity such as a sulfur compound, with a catalyst composition containing palladium and titanium dioxide in a hydrogenation zone under a condition effective to convert the highly unsaturated hydrocarbon to a less unsaturated hydrocarbon.		

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HYDROCARBON HYDROGENATION CATALYST AND PROCESS

FIELD OF THE INVENTION

This invention relates to a supported metal catalyst composition and to a process of using such supported metal catalyst composition for hydrogenating a highly unsaturated hydrocarbon in the presence of a sulfur impurity.

BACKGROUND OF THE INVENTION

By "consisting essentially of" herein it is intended to mean that the substance or combination of substances recited after this phrase does not include any further components which would materially affect the properties of the substances or combination of substances recited after this phrase.

Catalysts comprising palladium and an inorganic support are known catalysts for the hydrogenation of alkynes and/or diolefins. It is also generally known by those skilled in the art that a sulfur impurity such as a sulfur compound (such as H_2S , COS, mercaptans, and organic sulfides), when present during the hydrogenation of highly unsaturated hydrocarbons such as diolefins (alkadienes) or alkynes to less unsaturated hydrocarbons such as monoolefins (alkenes), can poison and deactivate hydrogenation catalysts. This is especially true in a depropanizer hydrogenation process because the feed stream from the depropanizer being sent to the acetylene removal unit (also referred to as "ARU") of such depropanizer hydrogenation process typically can contain low levels of a sulfur compound(s) with the possibility of transient concentration spikes in the level of such sulfur compound(s). Thus, the development of a catalyst composition and its use in processes for the hydrogenation of highly unsaturated hydrocarbons such as diolefins (alkadienes) or alkynes to less unsaturated hydrocarbons such as monoolefins (alkenes) in the presence of a sulfur impurity such as a sulfur compound would also be a significant contribution to the art and to the economy.

SUMMARY OF THE INVENTION

It is desirable to provide a palladium-containing catalyst composition which can be useful as a catalyst in the hydrogenation of a highly unsaturated hydrocarbon such as a diolefin and/or alkyne to a less unsaturated hydrocarbon such as a monoolefin wherein a sulfur impurity such as a sulfur compound is present.

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Again it is desirable to employ this catalyst composition in the hydrogenation of a highly unsaturated hydrocarbon such as a diolefin or an alkyne to a less unsaturated hydrocarbon such as a monoolefin wherein a sulfur impurity such as a sulfur compound is present. An advantage of this invention is that, in the presence of a sulfur impurity such as a sulfur compound, there is an increased or enhanced selectivity to a desired product such as a less unsaturated hydrocarbon.

According to a first embodiment of this invention, a catalyst composition is provided which comprises palladium and an inorganic support. The inorganic support can be a titanium dioxide, alumina, silica, zirconia, aluminosilicate (such as clays and/or zeolites), a spinel such as zinc aluminate, zinc titanate, magnesium aluminate, calcium aluminate, and combinations thereof. Such catalyst composition can be made by incorporating such inorganic support with palladium followed by drying and calcining.

According to a second embodiment of this invention, a process which can be used for hydrogenating a highly unsaturated hydrocarbon to a less un-saturated hydrocarbon in the presence of a sulfur impurity such as a sulfur compound is provided. The process comprises contacting a highly unsaturated hydrocarbon with hydrogen, in the presence of a catalyst composition and a sulfur impurity such as a sulfur compound, under a condition sufficient to effect a hydrogenation of the highly unsaturated hydrocarbon. The catalyst composition can be the same as the composition disclosed hereinabove in the first embodiment of this invention.

Other objects and advantages of the invention will be apparent from the detailed description of the invention and the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

As used in the present invention, the term "fluid" denotes gas, liquid, vapor, or combinations thereof. The term "substantial" or "substantially" generally means more than trivial. The term "saturated hydrocarbon" refers to any hydro-carbon which does not contain any carbon-to-carbon double bonds or carbon-to-carbon triple bonds. Examples of saturated hydrocarbons include, but are not limited to, ethane, propane, butanes, pentanes, hexanes, octanes, decanes, naphtha, and the like and combinations thereof.

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The term "highly unsaturated hydrocarbon" refers to a hydrocarbon having a triple bond or two or more double bonds between carbon atoms in the molecule. Examples of highly unsaturated hydrocarbons include, but are not limited to, aromatic compounds such as benzene and naphthalene; alkynes such as acetylene, propyne (also referred to as methylacetylene), and butynes; diolefins such as propadiene, butadienes, pentadienes (including isoprene), hexadienes, octadienes, and decadienes; and the like and combinations thereof.

The term "less unsaturated hydrocarbon" refers to a hydrocarbon in which the triple bond in the highly unsaturated hydrocarbon is hydrogenated to a double bond or a hydrocarbon in which the number of double bonds is one less, or at least one less, than that in the highly unsaturated hydrocarbon. Examples of less unsaturated hydrocarbons include, but are not limited to, monoolefins such as ethylene, propylene, butenes, pentenes, hexenes, octenes, decenes, and the like and combinations thereof.

The term "hydrogenation process" refers to a process which converts a highly unsaturated hydrocarbon such as an alkyne or a diolefin to a less un-saturated hydrocarbon such as a monoolefin or a saturated hydrocarbon such as an alkane. The term "selective" refers to such hydrogenation process in which a highly unsaturated hydrocarbon such as an alkyne or a diolefin is converted to a less unsaturated hydrocarbon such as a monoolefin without further hydrogenating the less unsaturated hydrocarbon to a saturated hydrocarbon such as an alkane. Thus, for example, when a highly unsaturated hydrocarbon is converted to a less un-saturated hydrocarbon without further hydrogenating such less unsaturated hydrocarbon to a saturated hydrocarbon, the hydrogenation process is "more selective" than when such highly unsaturated hydrocarbon is hydrogenated to a less un-saturated hydrocarbon and then further hydrogenated to a saturated hydrocarbon.

The composition of this invention comprises (a) palladium such as palladium metal, palladium oxide, or combinations thereof in which the palladium can be present as a "skin" distributed on or near the surface of an inorganic support material (preferably such inorganic support material is in the shape of a particle, pellet, extrudate, sphere, or the like) and (b) an inorganic support material selected from the

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group consisting of titanium dioxide, alumina, silica, zirconia, an alumino-silicate (such as clays and/or zeolites), a spinel such as zinc aluminate, zinc titanate, magnesium aluminate, calcium aluminate, and combinations thereof. The preferred inorganic support is titanium dioxide, also referred to as titania.

5 Generally, the composition comprises palladium in the range of from about 0.001 weight percent palladium based on the total weight of the composition to about 3 weight percent palladium, preferably in the range of from about 0.001 weight percent palladium to about 2.5 weight percent palladium, and, most preferably, in the range of from 0.001 weight percent palladium to 2 weight percent palladium and the
10 rest being inorganic support, preferably titanium dioxide. The composition can have any suitable shape such as spherical, cylindrical, trilobal, and combinations thereof. The particles of this catalyst generally have a size in the range of from about 1 mm to about 10 mm, preferably about 2 mm to about 8 mm. Generally the surface area of the catalyst as measured by the BET method (Brunauer, Emmett and Teller method)
15 employing N_2 is in the range of from about $0.5 \text{ m}^2/\text{g}$ to about $200 \text{ m}^2/\text{g}$, preferably in the range of from about $1 \text{ m}^2/\text{g}$ to about $100 \text{ m}^2/\text{g}$.

 The composition which is employed in the hydrogenation of this invention can be prepared by any suitable, effective method which results in an inorganic support incorporated with palladium. The palladium can be incorporated
20 (e.g., by ion exchange or impregnation) into, onto, or with the inorganic support. A preferred impregnation utilizes a soaking impregnation technique in which a substrate material (such as an inorganic support material) is soaked in a solution of the incorporating element(s) such that the solution volume is greater than the pore volume of the substrate material. The inorganic support can also be sprayed with an
25 impregnating solution comprising a palladium-containing compound. Preferably, the solvent of the impregnating solution is water or an alcohol such as ethanol or mixtures thereof. The weight ratio of the impregnating solution comprising a palladium-containing compound to the inorganic support can be any ratio that can produce the composition comprising palladium in the weight percent ranges disclosed herein
30 above.

 In a presently preferred catalyst preparation, a titanium dioxide support

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present in the form of pills sized 5.56 mm x 5.56 mm (7/32 inch by 7/32 inch) is contacted with an aqueous solution of palladium chloride by soaking to thereby provide a palladium-incorporated titanium dioxide, followed by drying and calcining, which results in the palladium-incorporated titanium dioxide composition of this invention.

Generally such drying is conducted at a temperature in the range of from about 35°C to about 160°C, preferably at a temperature in the range of from about 40°C to about 155°C, and, most preferably, at a temperature in the range of from 45°C to 150°C. The time period for conducting such drying is generally any period which results in a dried palladium-incorporated titanium dioxide composition. Generally, such time period for conducting such drying is at least about 0.5 hour. Preferably, such time period is in the range of from about 0.5 hour to about 50 hours, more preferably in the range of from about 1 hour to about 10 hours, and, most preferably, in the range of from 1.5 hours to 6 hours. Such drying is generally carried out at a pressure in the range of from about atmospheric i.e. about 101 kPa (about 14.7 pounds per square inch absolute) to about 689 kPa (about 100 pounds per square inch absolute (psia)), preferably about atmospheric.

Drying of the composition is then followed by calcining. Calcining of the composition is generally conducted at a temperature in the range of from about 200°C to about 1200°C, preferably in the range of from about 250°C to about 850°C, and, most preferably, at a temperature in the range of from 350°C to 700°C. Such calcining is generally conducted for a time period in the range of from about 0.5 hour to about 40 hours, preferably for a time period in the range of from about 0.75 hour to about 30 hours and, most preferably, for a time period in the range of from 1 hour to 20 hours. Such calcining is generally conducted at a pressure in the range of from about 7 pounds per square inch absolute (psia) to about 750 psia, preferably in the range of from about 7 psia to about 450 psia, and, most preferably, in the range of from 7 psia to 150 psia.

Examples of suitable palladium-containing compounds which can be used for incorporating the palladium of such palladium-containing compounds into, onto, or with an inorganic support include, but are not limited to, palladium bromide,

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palladium chloride, palladium iodide, palladium nitrate, palladium nitrate hydrate, tetraammine palladium nitrate, palladium oxide, palladium oxide hydrate, palladium sulfate, and the like and combinations thereof. The palladium can have any available oxidation state. The presently preferred palladium-containing compound is palladium chloride. Most preferably, hydrochloric acid is added to such palladium chloride (PdCl₂) to form a PdCl₄⁻² complex. Excess hydrochloric acid should be avoided.

According to the second embodiment of this invention, a hydrogenation process is provided. The hydrogenation process of this invention can comprise contacting a hydrocarbon-containing fluid which comprises one or more highly unsaturated hydrocarbon(s) such as an aromatic hydrocarbon(s), alkyne(s), and/or diolefin(s), in the presence of hydrogen and a sulfur impurity such as a sulfur compound, with the catalyst composition disclosed herein above to hydrogenate such one or more highly unsaturated hydrocarbon(s) to a less unsaturated hydrocarbon such as a monoolefin. The highly unsaturated hydrocarbon(s) is present in the hydrocarbon-containing fluid as an impurity generally at a level found in typical commercial feed streams. The highly unsaturated hydrocarbon(s) is present in the hydrocarbon-containing fluid generally in the range of from about 1 part by weight highly unsaturated hydrocarbon(s) per billion parts by weight hydrocarbon-containing fluid (i.e., about 1 ppb) to about 50,000 parts by weight highly unsaturated hydrocarbon(s) per million parts by weight hydrocarbon-containing fluid (i.e., about 50,000 ppm), typically at a level in the range of from about 10 ppb to about 40,000 ppm and, most typically, at a level in the range of from 100 ppb to 30,000 ppm.

The hydrocarbon-containing fluid of the hydrogenation process of this invention can also comprise one or more less unsaturated hydrocarbon(s) such as a monoolefin(s) and one or more saturated hydrocarbon(s) such as an alkane(s). These additional hydrocarbons can be present in the hydrocarbon-containing fluid at a level in the range of from about 0.001 weight percent to about 99.999 weight percent.

Examples of suitable alkynes include, but are not limited to, acetylene, propyne (also referred to as methylacetylene), 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and the like and combinations thereof. The presently preferred alkynes are acetylene and

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propyne.

The alkynes are primarily hydrogenated to the corresponding alkenes. For example, acetylene is primarily hydrogenated to ethylene; propyne is primarily hydrogenated to propylene; and the butynes are primarily hydrogenated to the corresponding butenes (e.g., 1-butene, 2-butenes).

Examples of suitable diolefins include those containing in the range of from 3 carbon atoms per molecule to about 12 carbon atoms per molecule. Such diolefins include, but are not limited to, propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyl-octadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes, cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene, and the like and combinations thereof.

Presently preferred diolefins are propadiene, 1,2-butadiene, 1,3-butadiene, pentadienes (such as 1,3-pentadiene, 1,4-pentadiene, isoprene), cyclopentadienes (such as 1,3-cyclopentadiene) and dicyclopentadiene (also known as tricyclo[5.2.1]^{2,6}deca-3,8-diene). These diolefins are preferably hydrogenated to their corresponding monoolefins containing the same number of carbon atoms per molecule as the diolefins. For example, propadiene is hydrogenated to propylene, 1,2-butadiene and 1,3-butadiene are hydrogenated to 1-butene and 2-butene, 1,3-pentadiene and 1,4-pentadiene are hydrogenated to 1-pentene and 2-pentene, isoprene is hydrogenated to methyl-1-pentenenes and methyl-2-pentenenes, and 1,3-cyclopentadiene is hydrogenated to cyclopentene.

Examples of suitable aromatic hydrocarbons include, but are not limited to, benzene, toluene, ethylbenzene, styrene, xylenes, and the like and combinations thereof.

Examples of suitable monoolefins include, but are not limited to,

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ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenenes, ethylcyclopentenenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and the like and combinations thereof.

Examples of suitable saturated hydrocarbons include, but are not limited to, methane, ethane, propane, butane, methylpropane, methylbutane, dimethylbutane, pentanes, hexanes, and the like and combinations thereof.

Furthermore, the hydrocarbon-containing fluid can contain in the range of from about 0.001 weight percent hydrogen to about 5 weight percent hydrogen, and up to 5000 parts per million by volume (ppmv) of carbon monoxide.

Examples of a sulfur compound(s) which can be present in the hydrocarbon-containing fluid as a sulfur impurity include, but are not limited to, hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS₂), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, organic trisulfides, organic tetrasulfides, and the like and combinations thereof, wherein each R can be an alkyl or cycloalkyl or aryl group containing 1 carbon atom to 10 carbon atoms. It is within the scope of this invention to have additional compounds (such as water, alcohols, ethers, aldehydes, ketones, carboxylic acids, esters and other oxygenated compounds) present in the hydrocarbon-containing fluid, as long as they do not significantly interfere with the hydrogenation process of a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon as described herein.

Generally, the sulfur compound(s) are present in the hydrocarbon-containing fluid in trace amounts preferably at a concentration of less than about 1000 parts per million by volume (ppmv) based on the total volume of the hydrocarbon-

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containing fluid, and generally at a concentration in the range of from about 0.5 ppbv sulfur to about 1000 ppmv sulfur (i.e., about 0.5 part by volume sulfur per billion parts by volume hydrocarbon-containing fluid to about 1000 parts by volume sulfur per million parts by volume hydrocarbon-containing fluid), preferably at a concentration in the range of from about 1 ppbv sulfur to about 500 ppmv sulfur, and most preferably, in the range of from 1 ppbv sulfur to 300 ppmv sulfur.

The hydrogenation process of this invention is generally carried out by contacting a hydrocarbon-containing fluid comprising of at least one highly unsaturated hydrocarbon, in the presence of hydrogen and a sulfur impurity such as a sulfur compound, with the catalyst composition of this invention. The hydrocarbon-containing fluid can be contacted by any suitable manner with the catalyst composition described herein which is contained within a hydrogenation zone. Such hydrogenation zone can comprise, for example, a reactor vessel.

The contacting step, of contacting the hydrocarbon-containing fluid with the catalyst composition, can be operated as a batch process step or, preferably, as a continuous process step. In the latter operation, a solid or fixed catalyst bed or a moving catalyst bed or a fluidized catalyst bed can be employed. Preferably, a fixed catalyst bed is employed. Any of these operational modes have advantages and disadvantages, and those skilled in the art can select the one most suitable for a particular hydrocarbon-containing fluid and catalyst composition.

The contacting step is preferably carried out within a hydrogenation zone, wherein is contained the catalyst composition, and under a condition that suitably promotes the hydrogenation process of a highly unsaturated hydrocarbon to a less unsaturated hydrocarbon as described herein. Such condition should be such as to avoid significant hydrogenation of a less unsaturated hydrocarbon(s) being initially present in the hydrocarbon-containing fluid to a saturated hydrocarbon(s) such as an alkane(s) or cycloalkane(s).

Generally, such condition comprises the presence of hydrogen, preferably hydrogen gas, in an amount in the range of from about 0.1 mole of hydrogen employed for each mole of highly unsaturated hydrocarbon present in the hydrocarbon-containing fluid to about 1000 moles of hydrogen employed for each mole of highly

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unsaturated hydrocarbon present in the hydrocarbon-containing fluid, preferably in the range of from about 0.5 mole to about 500 moles of hydrogen employed for each mole of highly unsaturated hydrocarbon present in the hydrocarbon-containing fluid and, most preferably, in the range of from 0.7 mole to 200 moles of hydrogen employed for each mole of highly unsaturated hydrocarbon present in the hydrocarbon-containing fluid.

Generally, such condition further comprises a temperature and a pressure necessary for the hydrogenation process of this invention depending largely upon the activity of the catalyst composition, the hydrocarbon-containing fluid composition, and the desired extent of hydrogenation. Generally, such temperature is in the range of from about 10°C to about 300°C, preferably in the range of from about 20°C to about 250°C, and, most preferably, in the range of from 20°C to 200°C. A suitable pressure is generally in the range of from about 103 kPa to about 13,780 kPa (about 15 pounds per square inch gauge (psig) to about 2000 psig), preferably in the range of from about 344 kPa to about 10,335 kPa (about 50 psig to about 1500 psig), and, most preferably, in the range of from 689 kPa to 6890 kPa, 100 psig to 1000 psig).

The flow rate at which the hydrocarbon-containing fluid is charged (i.e., the charge rate of hydrocarbon-containing fluid) to the hydrogenation zone is such as to provide a gas hourly space velocity ("GHSV") generally exceeding 1 liter/liter/hour. The term "gas hourly space velocity", as used herein, shall mean the numerical ratio of the rate at which a hydrocarbon-containing fluid is charged to the hydrogenation zone in liters per hour at standard condition of temperature and pressure ("STP") divided by the liters of catalyst composition contained in the hydrogenation zone to which the hydrocarbon-containing fluid is charged. Typically, the gas hourly space velocity of the hydrocarbon-containing fluid will be in the range of from about 1 to about 50,000 liters of hydrocarbon-containing fluid per liter of catalyst per hour (liter/liter/hour), preferably in the range of from about 750 to about 40,000 liter/liter/hour, and, most preferably, in the range of from 1000 to about 30,000 liter/liter/hour.

If it is desired to regenerate the catalyst composition of this invention after prolonged use in the hydrogenation process(es) described herein, the regeneration

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can be accomplished by calcining the catalyst in an oxidizing atmosphere such as in air at a temperature that does not exceed about 700°C to burn off carbonaceous and sulfur deposits. Optionally, the catalyst can be reimpregnated with palladium and heated as described above for the production of a fresh catalyst composition of this invention.

5 The following examples are presented to further illustrate this invention and are not to be construed as unduly limiting the scope of this invention.

EXAMPLE I

This example illustrates the preparation of various palladium-containing catalysts to be used in a hydrogenation process.

10 Catalyst A (Control) was a commercially available Pd/Ag/Al₂O₃ catalyst which contained about 0.016 weight percent Pd and about 0.048 weight percent Ag on 5.56 mm x 5.56 mm (7/32 inch by 7/32 inch) α-Al₂O₃ pellets. Control Catalyst A had a surface area measured by the BET method (Brunauer, Emmett and Teller method) employing N₂ of about 3 m²/g to about 5 m²/g and had been provided by United
15 Catalyst Inc. (UCI), Louisville, Kentucky under the product designation of "G83C". The G83C catalyst is a hydrogenation catalyst which is widely used in industry.

Catalyst B (Invention) was a palladium/titanium dioxide (Pd/TiO₂) catalyst which was prepared as follows: 100 grams of TiO₂ pills sized 5.56 mm x 5.56 mm (7/32 inch by 7/32 inch) provided by the Calsicat Catalyst Division of Engelhard
20 Company, Erie, Pennsylvania, under the product designation "Type B" were soaked for about 1 hour in 100 mL of an aqueous solution containing 0.02 gram of Pd (in the form of H₂PdCl₄) per gram of support (TiO₂ pills). The catalyst pills were stirred several times over the hour to ensure an even distribution of Pd. At the end of the hour the clear solution was decanted off, the pellets were dried at about 125°C for about 2
25 hours and then calcined in air for about 3 hours at about 538°C. The Pd/TiO₂ catalyst contained about 0.02 weight percent Pd.

EXAMPLE II

This example illustrates the performance of the catalysts described herein above in Example I in a hydrogenation process in the presence of sulfur
30 impurities such as sulfur compounds.

About 23 grams (i.e., about 20 cc) of each of the above described

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catalysts was placed in a stainless steel reactor tube having a 16 mm (0.62 inch) inner diameter and a length of about 46 cms (about 18 inches). The catalyst (resided in the middle of the reactor; both ends of the reactor were packed with 6 mL of 3 mm glass beads) was reduced at about 38°C for about 1 hour under hydrogen gas flowing at 12
5 liters per hour at 1378 kPa (200 pounds per square inch gauge (psig)). Thereafter, a hydrocarbon-containing fluid, typical of a feed from a front-end depropanizer of an ethylene plant, containing approximately (all by weight unless otherwise noted) hydrogen, 2.1%; methane, 22%; ethylene, 54%; propylene, 21%; acetylene, 4300 ppm; propadiene, 4300 ppm; propyne, 4300 ppm; and carbon monoxide, 300 ppm (by
10 volume) was continuously introduced into the reactor. The hydrocarbon-containing fluid was introduced into the reactor at a rate of 900 mL per minute at 1378 kPa (200 psig) translating to a gas hourly space velocity of about 2700 hour⁻¹. The reactor temperature was increased until the hydrogenation ran away, i.e., the uncontrollable hydrogenation of ethylene was allowed to occur. During the runaway, the heat of
15 hydrogenation built up such that the reactor temperature exceeded about 120°C (i.e., about 120°C to about 150°C). The reactor was then allowed to cool to room temperature, i.e., about 25°C, before data collection was started.

The reactor was then heated to about 82°C and a large concentration of carbonyl sulfide (COS) (approximately 300 mL at standard temperature and pressure
20 (STP) of 5000 ppmv COS in nitrogen) was passed over the catalyst. COS concentrations were then regulated by substituting part of the hydrogen flow (flowing at 12 liters/hour at 1378 kPa (200 psig)) with a blend of COS and hydrogen (COS/H₂ blend). The COS/H₂ blend was prepared as follows. A 5000 ppmv blend of COS in nitrogen was made by diluting 6.89 kPa (1 pound per square inch gauge (psig)) COS up to 1378
25 kPa (200 psia) COS with nitrogen in a 4 liter vessel to thereby provide a COS/N₂ blend. Next, 103 kPa (15 psia) of the COS/N₂ blend was diluted up to 3445 kPa (500 psia) with hydrogen in a gas cylinder. Under these dilutions, the theoretical COS concentration was approximately 150 ppmv. Due to the nature of the dilution, the concentration of COS could have been slightly higher. However, both runs using
30 Control Catalyst A and Invention Catalyst B used the same COS/H₂ blend with the same flow rates. The flow rates were set to deliver the hydrocarbon-containing fluid,

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hydrogen, and COS/H₂ blend to obtain a concentration of 17 parts COS per million parts by volume of hydrocarbon-containing fluid, hydrogen, and COS/H₂ blend (i.e., 17 ppmv COS).

The reactor was then "lined out" (i.e., acetylene and ethane concentrations remained essentially constant) at a temperature below 92 % conversion of the acetylene. Next, the temperature was increased and the reactor was again allowed to line out. This "lining out" process was repeated until all the acetylene was hydrogenated or the reaction was uncontrollable. The entire run was conducted in a continuous mode, with the catalyst always having hydrocarbon-containing fluid passing over the catalyst. The reactor effluent, i.e., the product stream, was analyzed by gas chromatography.

Ethane selectivity at various acetylene conversions in the presence of 17 ppmv COS are shown below in Table I. The term "ethane selectivity" refers to the amount of undesirable product (ethane) which was produced at various acetylene conversions relative to the initial acetylene concentration. A result greater than 100% indicates that the concentration of ethylene in the product stream was lower than the concentration of ethylene in the feed stream. Thus, when less ethane was produced, the catalyst was more selective or had a better selectivity to ethylene.

Table I							
Ethane Selectivity (%) at 17 ppmv COS							
Acetylene Conversion (%)	92	95	96	97	98	99	99.4 ^a
Catalyst A (Control)	78	113	151	205	b	b	b
Catalyst B (Invention)	53	48	60	70	90	138	242
^a Approximately 99.4 % conversion of acetylene is required to lower the acetylene concentration to 20 ppm which is typically referred to as the "cleanup". ^b Not obtained because of the uncontrollable hydrogenation of ethylene (i.e., a "runaway" reaction was occurring).							

Test data in Table I clearly show that Invention Catalyst B consistently

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produced less undesirable product, i.e., ethane, than Control Catalyst A at all acetylene conversions in the presence of 17 ppmv COS. In other words, Invention Catalyst B had better selectivity to ethylene than Control Catalyst A in the presence of a sulfur impurity. For example, at an acetylene conversion of 97 %, the ethane selectivity of Control Catalyst A was already at 205 % whereas the ethane selectivity of Invention Catalyst B was only at 70 %. In other words, Control Catalyst A was already producing almost three times as much ethane as Invention Catalyst B. Further, at an acetylene conversion of 97 %, Control Catalyst A was already producing so much ethane that further acetylene conversions of 98 %, 99 %, and 99.4 % could not be obtained because of the uncontrollable hydrogenation of ethylene (i.e., a "runaway" reaction was occurring). In contrast, Invention Catalyst B was able to obtain acetylene conversion up to 99.4 % (i.e., cleanup). The data clearly demonstrate that Invention Catalyst B did not deactivate as soon as Control Catalyst A in the presence of a sulfur impurity such as COS.

The performance of Invention Catalyst B, as compared to Control Catalyst A, is superior when comparing the ethane selectivity in the presence of a sulfur impurity. The improvement in catalyst performance is believed to be due to the novel process of using a catalyst prepared by incorporating a titanium dioxide support with palladium.

The results shown in the above examples clearly demonstrate that the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those inherent therein.

Reasonable variations, modifications, and adaptations can be made within the scope of the disclosure and the appended claims without departing from the scope of this invention.

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CLAIM

1. A process comprising contacting a hydrocarbon-containing fluid which comprises a highly unsaturated hydrocarbon, in the presence of hydrogen and a sulfur impurity, with a catalyst composition in a hydrogenation zone under a condition
5 effective to convert said highly unsaturated hydrocarbon to a less unsaturated hydrocarbon wherein said catalyst composition consists essentially of palladium and titanium dioxide.

2. A process according to claim 1, wherein said highly unsaturated hydrocarbon is selected from the group consisting of alkynes, diolefins, and
10 combinations thereof.

3. A process according to claim 2, wherein said alkynes are selected from the group consisting of acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and combinations thereof.

4. A process according to claim 3, wherein said diolefins contain in the range of from 3 carbon atoms per molecule to about 12 carbon atoms per molecule.

5. A process according to claim 4, wherein said diolefins are selected from the group consisting of propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene,
20 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyloctadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes,
25 cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene (also known as tricyclo[5.2.1]^{2,6}deca-3,8-diene), and combinations thereof.

6. A process according to claim 5, wherein said less unsaturated hydrocarbon is selected from the group consisting of ethylene, propylene, 1-butene,
30 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene,

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methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenenes, ethylcyclopentenenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations thereof.

7. A process according to claim 6, wherein said sulfur impurity is a sulfur compound selected from the group consisting of hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS₂), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, organic trisulfides, organic tetrasulfides, and combinations thereof, wherein said R can be an alkyl or cycloalkyl or aryl group containing 1 carbon atom to 10 carbon atoms.

8. A process according to claim 7, wherein said sulfur compound is present in said hydrocarbon-containing fluid at a concentration in the range of from about 0.5 ppbv sulfur to about 1000 ppmv sulfur (i.e., about 0.5 part by volume sulfur per billion parts by volume hydrocarbon-containing fluid to about 1000 parts by volume sulfur per million parts by volume hydrocarbon-containing fluid).

9. A process according to claim 8, wherein said sulfur compound is present in said hydrocarbon-containing fluid at a concentration in the range of from about 1 ppbv sulfur to about 500 ppmv sulfur (i.e., about 1 part by volume sulfur per billion parts by volume hydrocarbon-containing fluid to about 500 parts by volume sulfur per million parts by volume hydrocarbon-containing fluid).

10. A process according to claim 9, wherein said hydrocarbon-containing fluid further comprises a monoolefin.

11. A process according to claim 10, wherein said monoolefin is selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes,

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methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations thereof.

12. A process according to claim 11, wherein said hydrocarbon-containing fluid further comprises a saturated hydrocarbon selected from the group consisting of methane, ethane, propane, butane, methylpropane, methylbutane, dimethylbutane, pentanes, hexanes, and combinations thereof.

13. A process according to claim 12, wherein said hydrocarbon-containing fluid further comprises an aromatic hydrocarbon selected from the group consisting of benzene, toluene, ethylbenzene, styrene, xylenes, and combinations thereof.

14. A process according to any preceding claim wherein said condition comprises:

said hydrogen in an amount in the range of from about 0.1 to about 1000 moles of said hydrogen employed for each mole of said highly unsaturated hydrocarbon present in said hydrocarbon-containing fluid;

a temperature in the range of from about 10°C to about 300°C;

a pressure in the range of from about 103 kPa to about 13.8 MPa (about 15 pounds per square inch gauge (psig) to about 2000 psig); and

a charge rate of said hydrocarbon-containing fluid to said hydrogenation zone such as to provide a gas hourly space velocity in the range of from about 1 to about 50,000 liters of hydrocarbon-containing fluid per liter of catalyst per hour (liter/liter/hour).

15. A process according to claim 14, wherein said hydrogenation zone comprises a reactor vessel.

16. A process according to claim 15, wherein said palladium is present as skin on said titanium dioxide.

17. A process according to claim 16, wherein said palladium is present in

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said catalyst composition in an amount in the range of from about 0.001 to about 3 weight percent palladium.

18. A process comprising contacting a hydrocarbon-containing fluid which comprises a highly unsaturated hydrocarbon, in the presence of hydrogen and a sulfur impurity, with a catalyst composition in a hydrogenation zone under a condition effective to convert said highly unsaturated hydrocarbon to a less unsaturated hydrocarbon wherein said catalyst composition is prepared according to a process comprising:

incorporating titanium dioxide with palladium to thereby provide a palladium-incorporated titanium dioxide;
drying said palladium-incorporated titanium dioxide; and
calcining said palladium-incorporated titanium dioxide.

19. A process according to claim 18, wherein said incorporating comprises impregnating said titanium dioxide with an impregnating solution comprising a palladium-containing compound.

20. A process according to claim 19, wherein said palladium-containing compound is selected from the group consisting of palladium bromide, palladium chloride, palladium iodide, palladium nitrate, palladium nitrate hydrate, tetraammine palladium nitrate, palladium oxide, palladium oxide hydrate, palladium sulfate, and combinations thereof.

21. A process according to claim 20, wherein said palladium containing compound is palladium chloride and wherein hydrochloric acid has been added to said palladium chloride to form a PdCl_4^{2-} complex.

22. A process according to claim 21, wherein said drying comprises:
a temperature in the range of from about 35°C to about 160°C;
a time period for conducting said drying of at least about 0.5 hour; and
a pressure in the range of from about atmospheric to about 689 kPa
(about 100 pounds per square inch absolute).

23. A process according to claim 22, wherein said calcining comprises:
a temperature in the range of from about 200°C to about 1200°C;
a time period in the range of from about 0.5 hour to about 40 hours; and

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a pressure in the range of from about 48 kPa to about 5170 kPa (about 7 pounds per square inch absolute (psia) to about 750 psia).

24. A process according to claim 23, wherein said highly unsaturated hydrocarbon is selected from the group consisting of alkynes, diolefins, and combinations thereof.

25. A process according to claim 24, wherein said alkynes are selected from the group consisting of acetylene, propyne, 1-butyne, 2-butyne, 1-pentyne, 2-pentyne, 3-methyl-1-butyne, 1-hexyne, 1-heptyne, 1-octyne, 1-nonyne, 1-decyne, and combinations thereof.

26. A process according to claim 25, wherein said diolefins contain in the range of from 3 carbon atoms per molecule to about 12 carbon atoms per molecule.

27. A process according to claim 26, wherein said diolefins are selected from the group consisting of propadiene, 1,2-butadiene, 1,3-butadiene, isoprene, 1,2-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,2-hexadiene, 1,3-hexadiene, 1,4-hexadiene, 1,5-hexadiene, 2-methyl-1,2-pentadiene, 2,3-dimethyl-1,3-butadiene, heptadienes, methylhexadienes, octadienes, methylheptadienes, dimethylhexadienes, ethylhexadienes, trimethylpentadienes, methyloctadienes, dimethylheptadienes, ethyloctadienes, trimethylhexadienes, nonadienes, decadienes, undecadienes, dodecadienes, cyclopentadienes, cyclohexadienes, methylcyclopentadienes, cycloheptadienes, methylcyclohexadienes, dimethylcyclopentadienes, ethylcyclopentadienes, dicyclopentadiene (also known as tricyclo[5.2.1]^{2,6}deca-3,8-diene), and combinations thereof.

28. A process according to claim 27, wherein said less unsaturated hydrocarbon is selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes,

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ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes, trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations thereof.

29. A process according to claim 28, wherein said sulfur impurity is a sulfur compound selected from the group consisting of hydrogen sulfide, carbonyl sulfide (COS), carbon disulfide (CS₂), mercaptans (RSH), organic sulfides (R-S-R), organic disulfides (R-S-S-R), thiophene, organic trisulfides, organic tetrasulfides, and combinations thereof, wherein said R can be an alkyl or cycloalkyl or aryl group containing 1 carbon atom to 10 carbon atoms.

30. A process according to claim 29, wherein said sulfur compound is present in said hydrocarbon-containing fluid at a concentration in the range of from about 0.5 ppbv sulfur to about 1000 ppmv sulfur (i.e., about 0.5 part by volume sulfur per billion parts by volume hydrocarbon-containing fluid to about 1000 parts by volume sulfur per million parts by volume hydrocarbon-containing fluid).

31. A process according to claim 30, wherein said sulfur compound is present in said hydrocarbon-containing fluid at a concentration in the range of from about 1 ppbv sulfur to about 500 ppmv sulfur (i.e., about 1 part by volume sulfur per billion parts by volume hydrocarbon-containing fluid to about 500 parts by volume sulfur per million parts by volume hydrocarbon-containing fluid).

32. A process according to claim 31, wherein said hydrocarbon-containing fluid further comprises a monoolefin.

33. A process according to claim 32, wherein said monoolefin is selected from the group consisting of ethylene, propylene, 1-butene, 2-butene, isobutylene, 1-pentene, 2-pentene, methyl-1-butenes (such as 2-methyl-1-butene), methyl-2-butenes (such as 2-methyl-2-butene), 1-hexene, 2-hexene, 3-hexene, methyl-1-pentenenes, 2,3-dimethyl-1-butene, 1-heptene, 2-heptene, 3-heptene, methyl-1-hexenes, methyl-2-hexenes, methyl-3-hexenes, dimethylpentenes, ethylpentenes, octenes, methylheptenes, dimethylhexenes, ethylhexenes, nonenes, methyloctenes, dimethylheptenes, ethylheptenes, trimethylhexenes, cyclopentene, cyclohexene, methylcyclopentene, cycloheptene, methylcyclohexene, dimethylcyclopentenes, ethylcyclopentenes, cyclooctenes, methylcycloheptenes, dimethylcyclohexenes, ethylcyclohexenes,

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trimethylcyclohexenes, methylcyclooctenes, dimethylcyclooctenes, ethylcyclooctenes, and combinations thereof.

34. A process according to claim 33, wherein said hydrocarbon-containing fluid further comprises a saturated hydrocarbon selected from the group consisting of methane, ethane, propane, butane, methylpropane, methylbutane, dimethylbutane, pentanes, hexanes, and combinations thereof.

35. A process according to claim 34, wherein said hydrocarbon-containing fluid further comprises an aromatic hydrocarbon selected from the group consisting of benzene, toluene, ethylbenzene, styrene, xylenes, and combinations thereof.

36. A process according to any one of preceding claims 18-35, wherein said condition comprises:

said hydrogen in an amount in the range of from about 0.1 to about 1000 moles of said hydrogen employed for each mole of said highly unsaturated hydrocarbon present in said hydrocarbon-containing fluid;

a temperature in the range of from about 10°C to about 300°C;

a pressure in the range of from about 103 kPa to about 13780 kPa

(about 15 pounds per square inch gauge (psig) to about 2000 psig); and

a charge rate of said hydrocarbon-containing fluid to said hydrogenation zone such as to provide a gas hourly space velocity in the range of from about 1 to about 50,000 liters of hydrocarbon-containing fluid per liter of catalyst per hour (liter/liter/hour).

37. A process according to claim 36, wherein said hydrogenation zone comprises a reactor vessel; said palladium is present as skin on said titanium dioxide; and said palladium is present in said catalyst composition in an amount in the range of from about 0.001 to about 3 weight percent palladium.

38. A process of preparing a catalyst composition useful in contacting a hydrocarbon-containing fluid which comprises a highly unsaturated hydrocarbon, in the presence of hydrogen and a sulfur impurity, in a hydrogenation zone under a condition effective to convert said highly unsaturated hydrocarbon to a less unsaturated hydrocarbon, wherein said process comprises:

incorporating titanium dioxide with palladium to thereby provide a

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palladium-incorporated titanium dioxide;

drying said palladium-incorporated titanium dioxide; and
calcining said palladium-incorporated titanium dioxide.

39. A process according to claim 38, wherein said incorporating comprises
5 impregnating said titanium dioxide with an impregnating solution comprising a
palladium-containing compound.

40. A process according to claim 39, wherein said palladium-containing
compound is selected from the group consisting of palladium bromide, palladium
chloride, palladium iodide, palladium nitrate, palladium nitrate hydrate, tetraammine
10 palladium nitrate, palladium oxide, palladium oxide hydrate, palladium sulfate, and
combinations thereof.

41. A process according to claim 40, wherein said palladium containing
compound is palladium chloride and wherein hydrochloric acid has been added to said
palladium chloride to form a PdCl_4^{2-} complex.

15 42. A process according to claim 41, wherein said drying comprises:
a temperature in the range of from about 35°C to about 160°C;
a time period for conducting said drying of at least about 0.5 hour; and
a pressure in the range of from about atmospheric to about 689 kPa
(about 100 pounds per square inch absolute).

20 43. A process according to claim 42, wherein said calcining comprises:
a temperature in the range of from about 200°C to about 1200°C;
a time period in the range of from about 0.5 hour to about 40 hours; and
a pressure in the range of from about 48 kPa to about 5167 kPa (about 7
pounds per square inch absolute (psia) to about 750 psia).

25 44. A composition prepared according to the process of any one of
preceding claims 38-43.

45. A composition comprising palladium and titanium dioxide wherein said
composition is effective in converting under a condition a highly unsaturated
hydrocarbon to a less unsaturated hydrocarbon, in the presence of hydrogen and a
30 sulfur impurity, in a hydrogenation zone.

46. A composition according to claim 45, wherein said palladium is present

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in said composition in an amount in the range of from about 0.001 weight percent palladium based on the total weight of said composition to about 3 weight percent palladium.

47. A composition according to claim 46, wherein said palladium is present
5 as skin on said titanium dioxide.

48. A composition according to claim 47, wherein said composition has been subjected to drying and calcining.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US00/11021

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C07C 5/05, 5/03

US CL : 585/273, 275, 277

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 585/273, 275, 277

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,662,015 A (KOMATSU et al) 9 May 1972, the abstract, col. 1, lines 16-25, col. 3, line 44 thru col. 4, line 75, col. 5, lines 1-7, tables 1-3	1-48

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search

31 MAY 2000

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 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

THUAN D. DANG

 DEBORAH THOMAS *pat*
 PARALEGAL SPECIALIST

Telephone No. (703) 308-0661